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THE NICKEL-CATALYZED REACTION OF BUTADIENE WITH METHYLAMINE

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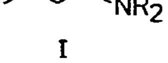
Summary

Butadiene reacts with methylamine in the presence of catalytic amounts of di-1,5-cyclooctadienenickel(0), tributylphosphine, and boron trifluoride etherate to give a mixture of *N*-methyldi-2,7-octadienylamine and *N*-methyl-*N*-3-(1,7-octadienyl)-2,7-octadiene-1-amino together with small amounts of *N*-methyl-1-octadieneamines and *N*-butenyl-*N*-methyloctadieneamines.

Butadiene reacts with secondary amines in the presence of various nickel catalysts to give mixtures of butenyl- (I, II) and octadienyl-amines (III, IV) [1]. We have recently demonstrated that compounds III and IV are formed exclusively, in high yields, when a catalyst prepared from nickel(II) acetylacetonate, triphenylphosphine and triethylaluminium or from di-1,5-cyclooctadienenickel(0), triphenylphosphine and a Lewis acid, e.g. triethylaluminium or boron trifluoride etherate is used [2].

In the analogous reaction with primary amines only low yields of dibutenyl-, butenyloctadienyl-, and dioctadienyl-amines have so far been obtained [1,3]. This is a serious limitation of the amination reaction and it is also puzzling from a mechanistic point of view, particularly since the palladium-catalyzed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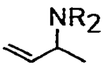
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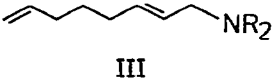
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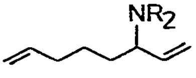
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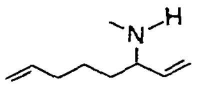

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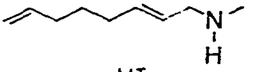

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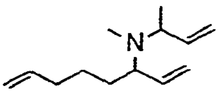

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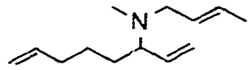

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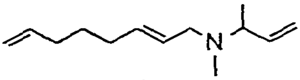

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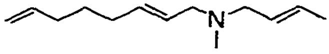

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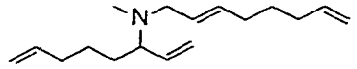

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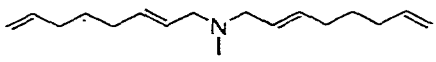


XII

amination of butadiene with benzylamine has been reported [4]. In that particular case the catalyst was prepared from palladium(II) acetylacetonate, triethylaluminium and tributylphosphine, and was generally used in the presence of various "additives" like trifluoroacetic acid, acetic acid and diethylammonium chloride. We have therefore investigated the nickel-catalyzed reaction between methylamine and butadiene in greater detail, and have found that high yields of dioctadienylamines may in fact be obtained under rather narrowly defined conditions.

Results

Butadiene reacts with methylamine in the presence of di-1,5-cyclooctadienenickel(0), tributylphosphine and boron trifluoride etherate in tetrahydrofuran (THF) to give a mixture of the compounds VII—XII together with small amounts of compounds V and/or VI (MS). Although the reaction has not been fully optimized, a total yield of about 80% of the desired compounds XI and XII has been obtained.

In the absence of Lewis acid or when triethylaluminium is used, no amina-

TABLE 1

REACTIONS OF METHYLAMINE (20 mmol) WITH BUTADIENE (80—90 mmol) CATALYZED BY $Ni(COD)_2$ (0.5 mmol), PBu_3 (1.5 mmol) AND BORON TRIFLUORIDE ETHERATE (0.8 mmol)

Temperature (°C)	Time (h)	Relative yields						Total yield [c] (%)
		VII	VIII	IX	X	XI	XII	
—50 [a]	20							14
—50 [a]	70	8	5	17	3	34	33	96
20	20	7	4	14	2	32	41	85
20 [b]	20	2	1	15	2	31	49	25
60	4	2	1	13	3	32	49	99
100	2	2	2	15	6	26	49	73

[a] The reaction mixture were allowed to reach room temperature within 20 h and thereafter kept at room temperature. [b] 880 mmol butadiene. [c] Based on methylamine.

tion takes place. This is also true when triphenylphosphine is used as ligand in place of tributylphosphine. The choice of solvent appears less critical and THF may be replaced by toluene.

Certain definite trends in the reaction are observed. The relative yields of the butenyloctadienylamines VII and VIII decrease with increasing temperature while the yield of the butenyloctadienylamine IX remains constant and that of X increases slightly at 100°C. The 2-butenyl adducts VII and IX dominate over the corresponding 1-butenyl adducts VIII and X and only a small decrease of the 2-butenyl/1-butenyl adduct ratio is observed with increasing temperature. This type of dominance is not observed for the dioctadienyl adducts but the ratio of XII/XI increases with increasing temperature (Table 1). The ratio also increases at low conversion and with a high butadiene-catalyst ratio.

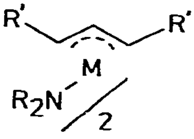
We have observed no isomerization of the branched dioctadienylamine XI to the linear isomer XII under the reaction conditions. In the presence of bis(triphenylphosphine)palladium(II) chloride and triethylaluminium, however, XI is totally isomerized to XII within three days at room temperature. As might be expected, the reaction rate is fairly low at —50°C and increases with the temperature. At temperature above 60°C side reactions tend to decrease the yield of amination products (Table 1).

Finally, both rate and yields appear to be only moderately affected when the ligand/nickel ratio is varied from 1/1 to 4/1.

Discussion

The mechanism of the nickel-catalyzed amination of butadiene is not completely clear but π-allylnickel complexes are very likely intermediates [1]. The octadienyl moiety probably stems from the bis-π-allyl complex XIII and the butenyl products from a π-crotyl complex of the type XV. In both cases, amination products could be formed either by nucleophilic attack by an external amine or by the internal transfer of the coordinated amine or perhaps amide. Experimental studies on π-allylpalladium systems indicate external attack by the amine [5,6] on a positively charged system. A charged intermediate is also indicated [2,7] for nickel. Amide complexes of the type XVI (M = Pd), which should be formed by deprotonation of amine complexes react slowly to give low yields of amines [8]. When M = Ni an amine is formed only when R = H; with R = CH_3 the π-allyl group is eliminated as 1,3-pentadiene [9].

These facts, together with stereochemical studies that are in progress, indicate that external attack is preferred also for the π-allylnickel complexes. Likely intermediates are the positively charged complexes XIV for the octadienyl products and XV for the butenyl products. We have previously suggested that secondary amines yield the charged complex XIV by protonation of the bis-π-



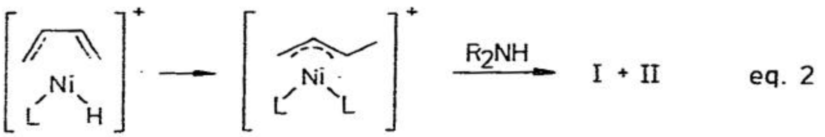
XVI

XIII XIV

allyl complex XIII by the amine-triethylaluminium complex (eq. 1) [2]. A similar type of mechanism should also apply to the reaction with primary amines, but no reaction was obtained with triethylaluminium as the Lewis acid. The reason is probably that while secondary amines yield fairly stable complexes with triethylaluminium the primary amine complexes decompose rapidly at room temperature according to eq. 3 [10]. The product from e.g. ethylamine is a polymeric ethylaluminium-ethylamide, which may well be a poor catalyst for the protonation of π-allyl complexes. In contrast, boron trifluoride forms stable complexes also with primary amines [11]. These complexes are sufficiently acidic ($pK_a \cong 7$) to be able to protonate a bis-π-allyl complex, and boron trifluoride is expected to be an eficient amination cocatalyst even with primary amines in accordance with experimental observations *.

Methylamine and dimethylamine also have different requirements for the auxiliary ligand L. The basicity of the ligand appears to be crucial. With a secondary amine, triphenyl- and tributyl-phosphine both work but not the less basic triphenyl phosphite. With methylamine only the strongest base, tributylphosphine, works. An attractive explanation is that a basic ligand L in the complex XIII is required to facilitate protonation. However, since the methylamine adduct is the strongest acid; this explanation is unlikely. A more reasonable explanation is therefore that the phosphine has to compete with free amine as the ligand L in XIII. If the amine becomes coordinated to any considerable extent, amide complexes XVII could form, which should yield octatriene rather than an amination product [9]. The coordination of methylamine should be more efficient than that of a secondary amine for steric reasons, which explains the need for a more strongly coordinating auxiliary ligand.

Another difference between the reaction with methylamine and secondary amines is that the latter can be made to yield only octadienylamines while methylamine, even under optimum conditions (so far) gives 20—30% butenyl-octadienyl adducts in addition to dioctadienyl adducts. The reason may be the



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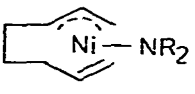
* This may also explain why amination with dimethylamine gives a poor yield of octadienylamines at room temperature and a higher yield at lower temperature when triethylaluminium is used as the Lewis acid [2]. With boron trifluoride etherate, however, a high yield is obtained at room temperature [12].

$$R\overset{+}{N}H_2-\overset{-}{Al}Et_3 \longrightarrow RNH-AlEt_2 + EtH \qquad \text{eq. 3}$$



XVII

greater acidity of the methylamine-boron trifluoride complex. It is reasonable to assume that the octadienyl adducts are formed via the bis-π-allyl complex XIII and the butenyl adducts via nickel hydride and π-crotylnickel (XIV). The stronger the acid the higher, presumably, is the rate of protonation of nickel(0) in competition with the formation of XIII from butadiene and nickel(0).

The product pattern requires some further comment. In the palladium-catalyzed reaction of benzylamine with butadiene, only linear products are obtained [4]. In contrast, the nickel-catalyzed reaction gives branched products like XI, both with methylamine and secondary amines. The explanation is probably that the branched products are kinetically favoured while the linear products are thermodynamically favoured. This is indicated by experiments with π-crotylpalladium complexes [8] and also by the fact that palladium(0) catalyzes the isomerization of branched to linear products at room temperature while nickel(0) is ineffective even at 80°C. The branched products observed with nickel are thus probably the products formed by kinetic control. With methylamine, the branched isomers dominate among the butenyloctadienyl adducts, e.g. VII/VIII ~ 2/1 and IX >> X at all temperatures below 60°C.

Among the dioctadienyl products, this dominance is less pronounced. Approximately equal amounts of XI and XII are formed. The ratio XII/XI is increased from about 1 at low temperature to 1.9 at 100°C (Table 1). The ratio is not greatly affected by the phosphine/nickel ratio. Although the product ratio is difficult to control, this is not crucial if the desired product is the linear isomer XII, since this may be obtained by palladium-catalyzed isomerization.

Experimental

Gas chromatography was performed on a Varian 1400 instrument using a 2.1 m × 2 mm column of 20% Apiezon L + 10% KOH on Chromosorb W (for analytical runs) and on a Pye 104 instrument using a 3 m × 19 mm column of 20% Apiezon L + 10% KOH on Chromosorb W (for preparative runs). NMR spectra were recorded on a Bruker WP 200 spectrometer (TMS internal standard), mass spectra on an LKB 9000 instrument and IR spectra on a Perkin—Elmer 257 spectrometer.

Commercial samples of all reagents were used without further purification. PA grade toluene was dried with molecular sieves and THF was distilled from potassium and benzophenone. All reactions were performed under purified nitrogen. A glove-bag was used for manipulations of di-1,5-cyclooctadiene-nickel.

General procedure of the amination reaction

Di-1,5-cyclooctadienenickel (0.5 mmol) was placed in a Fisher and Porter glass autoclave equipped with a magnetic stirrer. The apparatus was flushed with nitrogen and cooled to approximately —75°C. Butadiene (80—800 mmol) was distilled into the apparatus. Methylamine (20 mmol) in THF or toluene (ca. 5 ml), tributylphosphine (0.5—2 mmol) and boron trifluoride etherate (0.8 mmol) were added. The mixture was stirred at various temperatures and for the time indicated for the various runs. The product mixtures were analyzed by GLC with tetradecane as an internal standard. A rough separation of the dioctadienylamines from the butenyloctadienylamines could be made by extraction, since the hydrochlorides of the dioctadienylamines are sparingly soluble both in diethyl ether and in the acidic water phase. Pure products were obtained by preparative GLC.

Mass spectra showed the molecular ions of all compounds. The stereochemistry of the double bonds of all adducts was assigned as *trans* on the basis of strong absorption in the 970 cm^{-1} region of the IR spectra and the lack of absorption at 650—700 cm^{-1}. The NMR spectrum of compound VII showed absorption at δ 5.6—5.9 (m, 3 H), 4.9—5.2 (m, 6 H), 3.27 (dq, J 7 and ca. 1 Hz, 1 H), 3.1 (m, 1 H), 2.16 (s, ca. 1.5 H), 2.15 (s, ca. 1.5 H), 2.0—2.1 (m, 2 H), 1.3—1.7 (m, 4 H) and 1.11 (apparent t, J 7 Hz, 3 H), that of compound VIII at δ 5.4—5.9 (m, 4 H), 4.9—5.2 (m, 4 H), 2.8—3.1 (m, 3 H), 2.17 (s, 3 H), 2.0—2.1 (m, 2 H), 1.7 (dd, J 6 and 1 Hz, 3 H) and 1.3—1.7 (m, 4 H), that of compound IX at δ 5.7—5.9 (m, 2 H), 5.3—5.6 (m, 2 H), 4.9—5.1 (m, 4 H), 3.11 (dq, J 7 and ca. 1 Hz, 1 H), 3.0 (AB part of ABX spectrum, 2 H), 2.17 (s, 3 H), 2.0—2.15 (m, 4 H), 1.47 (apparent quintet, J 7 Hz, 2 H) and 1.14 (d, J 7 Hz, 3 H), that of compound X at δ 5.6—5.9 (m, 2 H), 5.4—5.6 (m, 3 H), 4.9—5.05 (m, 2 H), 2.9 (m, 4 H), 2.16 (s, 3 H), 2.0—2.1 (m, 4 H), 1.68 (d, J 5 Hz, 3 H) and 1.47 (apparent quintet, J 7.5 Hz, 2 H), that of compound XI at δ 5.4—5.9 (m, 5 H), 4.9—5.2 ((m, 6 H), 2.8—3.1 (m, 3 H), 2.17 (s, 3 H), 2.0—2.1 (m, 6 H) and 1.3—1.6 (m, 6 H) and that of compound XII at δ 5.7—5.9 (m, 2 H), 5.4—5.6 (m, 4 H), 4.9—5.0 (m, 4 H), 2.92 (d, J 5.4 Hz, 4 H), 2.17 (s, 3 H), 2.0—2.1 (m, 8 H) and 1.47 (apparent quintet, J 7.5 Hz, 4 H).

Acknowledgements

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